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Chemistry of a Biscarborane Dithiol and Its Nickel (II) Complex

Tyler Hemingway

CHEMISTRY OF A BISCARBORANE DITHIOL AND ITS NICKEL(II) COMPLEX

by

Tyler Hemingway

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Accepted by:

Dmitry V. Peryshkov, Director of Thesis

Aaron Vannucci, Reader

Cheryl L. Addy, Vice Provost and Dean of the Graduate School

DEDICATION

I would like to dedicate this work to my parents. I could not have accomplished any of my goals without their wisdom and support to guide me every step of the way.

ACKNOWLEDGEMENTS

I would like to acknowledge my professor Dr. Dmitry Peryshkov. I was able to accomplish what I have in my program through his guidance and immense knowledge of chemistry. Thank you for all of your help through my time here.

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Finally, I would like to thank my group members, and all of the other graduate students that I have met here. I will truly miss all of you, and I wish all of you the best of luck as you finish your programs.

ABSTRACT

Neutral biscarborane dithiol and its anionic dithiolate form were successfully synthesized and structurally characterized. The C–C intracluster bond lengths were found to be responsive to the electron density on the cluster. Introduction of two thiol groups on biscarborane led to the significant increase of intracluster C–C bond lengths compared to those of unsubstituted biscarborane. Furthermore, the anionic dithiolate form had even longer C–C cluster bonds. This comparison shows electronic effect of substituents attached to carbon atoms of biscarborane on the strength of its C–C bonds. Additionally, a novel Ni complex was obtained using this dithiolate as a ligand. This complex was shown to use the redox-active biscarborane dithiolate ligand to store electrons.

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CHAPTER 1

INTRODUCTION

1.1 Carboranes

Boron is unable to form a stable octet by forming bonds with its valence electrons. Due to this electron deficiency, boron can enter unusual bonding situations to complete its octet. One such bonding situation that has gained much attention can be found in carboranes. Carboranes are inorganic three-dimensional cluster molecules consisting of carbon, boron, and hydrogen atoms.[1] As a result of their unique properties such as high thermal stability, aromatic-like delocalization of electrons, highly acidic C-H bonds, and high concentration of boron atoms in each molecule, icosahedral *closo*-$C_2B_{10}H_{12}$ carboranes have been studied for a variety of applications, such as catalysis,[2] boron neutron capture therapy,[3] luminescence,[4] and polymers.[5] While the C-H and B-H bonds are normal covalent bonds, the C-B and C-C bonds in a carborane consist of 3 center-2 electron bonds. Many different carboranes exists, but the 12-vertex, icosahedral carborane clusters of the formula $C_2B_{10}H_{12}$ are the ones that have been the most explored due to their high stability in comparison to other carboranes.[1] (Figure 1.1) There are three isomers of the icosahedral carboranes: *ortho*-, *meta*-, and *para*-, which are named based on the location of the carbons in the carborane cage.[1]

Along with different isomers, carboranes can open up the cage either through the breaking of bonds by the reduction of the cluster or through the removal of one or more of

its vertices, which is called deboronation.[6] When the cluster has not opened at all, the structure is in its *closo*- form, which is the icosahedral shape (Figure 1.1). If one bond within the closo- structure breaks or a vertex is removed, then the cluster is in its *nido*- form. Subsequent loss of vertices will result in the *arachno*- and *hypho*- forms of carborane.[1]

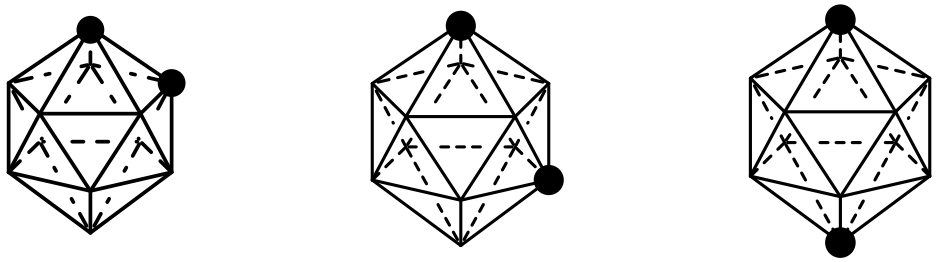
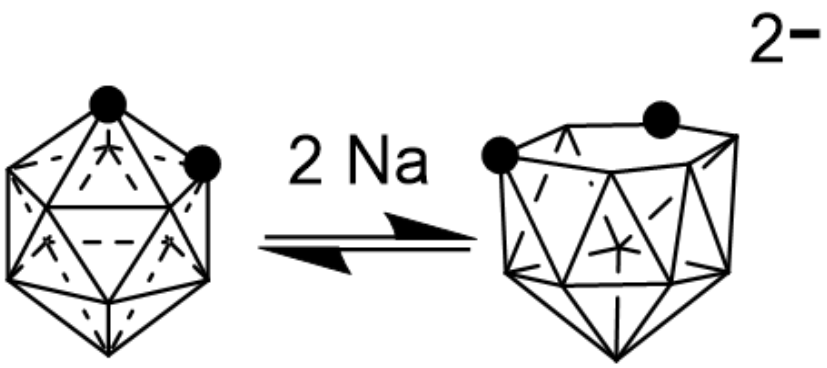


Figure 1.1: Three isomers of 12-vertex carboranes. Empty vertices represent B-H bonds, and black dots represent C-H bonds.[1]

Carboranes have gained attention due to their interesting properties that are caused by the electron deficiency of the borons of the cage and their activation of the B-H and C-H bonds. This deficiency causes the C-H to be significantly more acidic than other C-H bonds and leads to a relative ease of deprotonation of the carbons of the cluster through the use of a strong base.[1] This deprotonation leads to the formation of carbanions on the cage, which act as strong nucleophilic centers on the cluster. These nucleophilic centers can readily react with a variety of substrates. As a result, a variety of C-functionalized carboranes can be formed. Many different substituted carboranes have been previously reported, including dihydroxy forms for each isomer of 12-vertex-closo-carborane.[7] Although the C-H bonds are relativity acidic, the B-H bonds are much more stable. However, even these bonds can still be activated. One method to activate B-H bonds is a

process similar to Friedel-Crafts acylation using $AlCl_3$.[1] Another technique to activate these bonds is through the use of transition metals. Due to the three-dimensional nature of the carborane cluster, if a carborane is attached to a metal center, the hydrogen of one of the B-H bonds may be close enough to the metal center for a binding interaction to occur between the boron and the metal center.[8]

The electron deficiency of the *ortho*-carborane cluster also allows them to easily accept two more electrons into the cluster. When this occurs, the C-C bond within the cluster breaks and the cluster opens up into its nido-form.[9] Since both carbons are still present on the molecule in this form, this reduction can easily be reversed to revert the cluster back to its *closo*-state. Thus, carboranes can undergo a reversible two-electron reduction (Figure 1.2).[10] This reduction creates an open space for new atoms to be incorporated into the cluster, allowing for a variety of new carborane clusters with new heteroatoms incorporated within the cluster.[11,12]



Scheme 1.1: Reduction of *ortho*-carborane. Empty vertices represent B-H bonds, and black circles represent C-H bonds.[10]

1.2 Biscarborane

Although carboranes have received much attention since their discovery, bis-carborane has received relatively little attention. The synthesis of biscarborane was originally reported by Hawthorne and coworkers in 1964, but the low yield of their reaction hindered any further advancements.[13] In 2008, however, Ren and coworkers reported a new method to synthesize biscarborane in an appreciable yield, which has allowed the molecule to be studied more closely.[14] Biscarborane is a derivative of *ortho*-carborane in which two carborane clusters are bonded together through a single C-C bond (Figure 1.3). When bound to a metal center, biscarborane generally acts as a bidentate dianionic ligand, similar to *ortho*-carborane.[15] However, due to comprising of two linked carborane cages, biscarborane has shown interactions both within a metal complex and as a standalone molecule that make it very interesting to study.

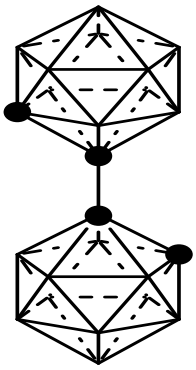
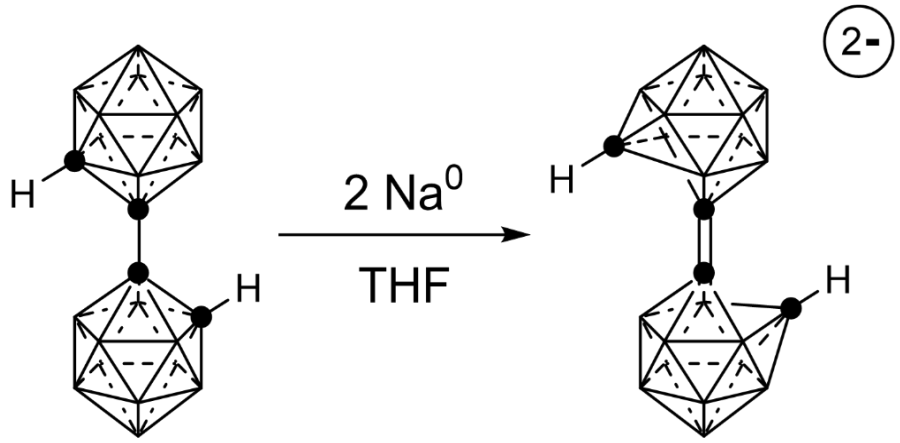


Figure 1.2. Molecular structure of biscarborane[1]

As stated previously, when an *ortho*-carborane cage accepts two electrons into its cluster, the C-C bond within the cluster will break, and the cluster will be in its *nido*- form.[1] As a result, it was speculated that, when biscarborane is reduced by two electrons, one of

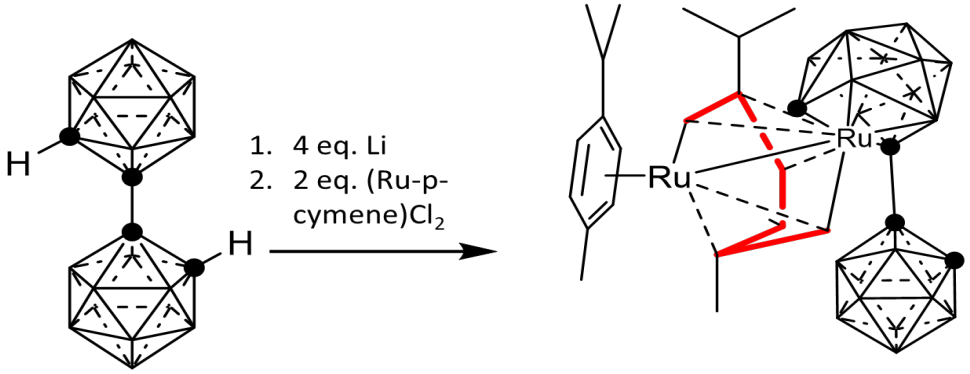
its clusters would convert to the *nido*- form, and the other would remain in the *closo*- form. However, upon the 2-electron reduction of biscarborane, it was observed that both clusters open from the *closo*- to the *nido*- form, and a double bond forms between the carborane cages (Figure 1.4).[16] Upon reducing biscarborane by two more electrons, the double bond between the two clusters converts to a single bond.[16] This observation shows that, upon reduction, the two clusters will distribute the electrons between each other in a resonance like manner. Thus, the two clusters do not function like two separate carboranes; they instead function together, which leads to interactions such as this distribution of electrons between the clusters.



Scheme 1.2. Reduction of biscarborane[16]

Biscarborane also shows some of these unique interactions in metal clusters. One example occurs from the formation of a metallacarborane, which is a carborane that has a metal incorporated into the cluster itself.[17] By reducing biscarborane by four electrons and adding ruthenium *para*-cymene, something unusual happens. One ruthenium becomes part of one of the clusters and the other one coordinates to the *para*-cymene of the first ruthenium cluster. Additionally, the benzene ring of the cymene molecule was reduced,

and one of its C-C bonds were broken, and the second cluster was unchanged. A mechanism was proposed that, after the second cluster is reduced, it acts as an electron reservoir and donates its extra electrons to the benzene ring of the first cymene.[18] This donation causes the ring to be reduced and ultimately causes the C-C bond cleavage observed (Scheme 1.3).[18] This unique interaction further shows how the carborane clusters of biscarborane can interact to create many interesting interactions.



Scheme 1.3: Aromatic C-C bond cleavage in a biscarborane structure. The red bonds indicate the bonds that comprised a benzene ring before cleavage.[18]

1.3 Flow Batteries

As the demand for more energy increases throughout the world, alternative, renewable energy sources versus fossil fuels become ever more necessary. Solar and wind energy have shown to be promising alternatives to fossil fuels,[19] but the intermittency of these fuel sources requires proper storage capabilities of these fuel sources in order for them to be efficient energy sources compared to the nonintermittent fossil fuels. Traditional solid electrode batteries have proven to be an inefficient method of storage for these renewable fuels. This is mainly due to the scaling of the power capacity and energy capacity

of the battery. These capacities are combined in such a way that, when the energy capacity is scaled up, then the power capacity must also be scaled up.[20] As a result, whenever more energy needs to be stored in a battery, that same battery will also use energy more quickly, and the battery will not last long. This results in an insufficient energy-to-power ratio for these batteries since batteries need to last for long periods of time to act as a primary power source.[20] Thus, an alternative storage method to solid electrode batteries is required for storage of intermittent energy sources.

Other storage methods such as the sodium sulfur battery[21] and lead-acid batteries[22] are all being examined to store these energy sources. Flow batteries are another promising method of energy storage. Flow batteries consist of two electrolytes dissolved in separate solutions in different containers, an electrode, a protective membrane to separate the two electrolytes at the electrode, and a method to pump the electrolyte in and out of the chamber containing the electrode.[23] The two electrolytes are named the catholyte, which will be reduced to higher energy state, and the anolyte, which will be oxidized to a higher energy state. When energy needs to be stored in the battery, the electrolytes are pumped into a chamber that contains the electrode with a divider that separates the two electrolytes. As energy is generated, a redox reaction will convert each electrode into their respective higher energy states and convert the electrical solar or wind energy into chemical energy, and the electrolytes will then be pumped back into their respective chambers.[23] The electrolytes can then be stored until the energy supply is needed. When the energy is needed, the electrolytes are then pumped back into the chamber containing the electrode, and a reverse redox reaction at the electrode will convert the chemical energy back into electrical energy and bring the electrolytes back down to their respective lower energy states.[23] The

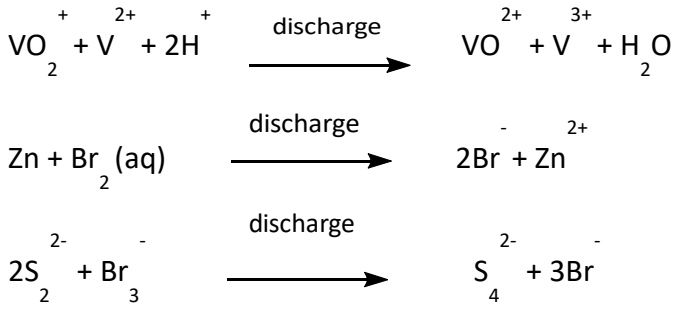
advantage of this system is the separation of the power supply (electrode) from the energy supply (electrolyte). Thus, the energy supply can be scaled up without the need to scale up the power supply. The power can then be scaled to meet the demands of the output, and the battery will last longer as a result.[24]

The use of flow batteries for storing energy also comes with some challenges since the system relies on two electrolytes to be both oxidized and reduced, both electrolytes used in this reaction must have at least one reversible reduction peak. Additionally, the electrolyte must be stable in solution for a long period of time in order to properly store energy. To get the most potential charge into a system, electrolytes with multiple reversible reduction potentials are preferable. If these batteries are to be used for a long period of time, then all of the components, particularly the electrolytes that repetitively undergo redox reactions, must be stable for long periods of time.[25] Finally, for these products to be commercialized, it is important that the conditions for the reaction are as mild as possible. In particular, strong acids should be avoided because, in addition to their high corrosiveness, free protons in the system may be reduced to hydrogen gas, which will build up in this closed system and eventually cause the electrode to rupture.[24]

One heavily examined flow battery system is an all vanadium system (Scheme 1.4), which utilizes the diverse oxidation states of vanadium such that vanadium compounds act as both the catholyte and the anolyte.[26] The main issue with this system is the need for strong sulfuric acid. The vanadium compounds used are not soluble in organic solvents, so sulfuric acid is necessary to dissolve the compound, which could lead to the issues of corrosivity and hydrogen evolution previously described. Along with these issues,

this system also provided limited voltage output since the potentials of the vanadium compounds were close together and high costs due to the cost of vanadium compounds.[23]

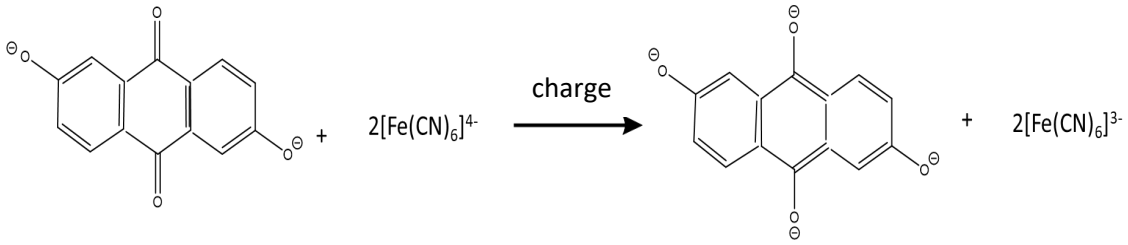
Due to the high cost of vanadium, other systems that utilized cheaper materials were also examined, but these systems also had their own issues. One battery uses sodium bromide and sodium polysulfide as electrolytes[27] (Scheme 1.4), but this system is still run in an aqueous medium which has the same hydrogen evolution issue as the vanadium system. Another zinc-bromine system was also examined (Scheme 1.4), but this system usually runs in an aqueous medium.[28] Additionally, the use of corrosive bromine would be a health concern and limit this system's commercial use.[24]



Scheme 1.4. Examples of flow battery systems[23]

One flow battery system that has been described recently involves the use of quinone as one of the electrolytes. (Scheme 1.5) This system relieves many of the potential issues of the previously described flow battery systems. First, since the quinone easily dissolves in many organic solvents and is nontoxic, this system does not need to be done in an aqueous solution, thus removing the potential issue of hydrogen evolution and the toxicity issue.[24] As shown in the reaction scheme, quinones do have a reversible two electron reduction, which makes them more desirable for electrolytes as stated

previously.[29] One trait of quinones which really sets them apart is the way that their redox reaction occurs. In all previous systems, both electrolytes had to completely break apart into two separate molecules or form new bonds with separate molecules. Quinones, on the other hand, do not break any bonds and only accept and donate electrons through resonance.[24] Since new bonds do not need to form, the redox of a quinone should perform faster than other reactions, and the quinone should be more stable through repeated redox reactions.



Scheme 1.5. Quinone flow battery system[24]

Since quinones have properties that are appealing for flow battery electrolytes, we wanted to explore other compounds that have quinone-like redox chemistry. Namely, we wanted to explore the use of carboranes as electrolytes for flow batteries. As stated previously, when the carborane cage is reduced by two electrons, the C-C bond within the cluster breaks and opens one face of the cluster. Although carboranes do break a bond, both carbons remain part of the cluster, so the bond is easily reformed when the two extra electrons are removed from the cluster. Thus, the reduction of these clusters is usually easily reversible similar to quinones. Additionally, carboranes are stable molecules, so we hypothesize that they should last a long time through these redox reactions before decomposition. In this work, we hypothesize that carborane compounds could be potential candidates for use as electrolytes in flow batteries.

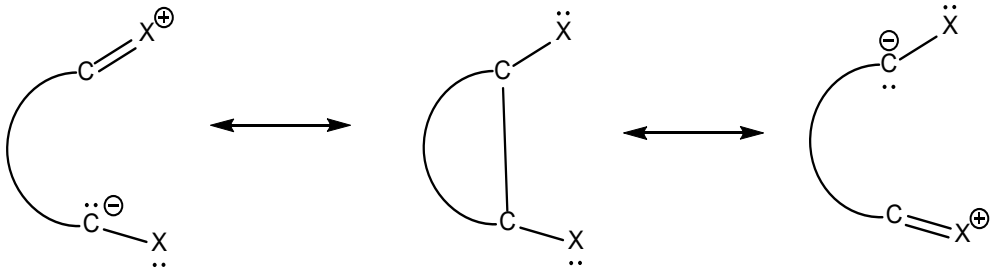
DFT calculations done on theoretical models of several substituted *o*-carborane molecules found that the C-C bond distance of the cluster increased in most of these substituted *o*-carboranes compared to unsubstituted *o*-carborane. This bond distance increase was found to be due to negative hyperconjugation.[30] Substituents found on the carbons act as electron donors to the carborane cage. The HOMO of *o*-carborane, however, is a σ* C-C antibonding orbital. As the substituents donate electron density to the carborane cage, this antibonding orbital begins to fill, which will weaken the C-C bond of the cage and cause it to elongate.[30] Additionally, substituents that are better electron donors elongated the C-C bond more than substituents with less donating ability.[31] Thus, the overall donating ability of different substituents can be compared by examining the C-C bond distance. Additionally, this model also predicts that bond elongation is much more pronounced for the anionic form of each substituted biscarborane due to the enhanced donating ability of the anionic form of each substituent. This model is supported by Li and coworkers when diamino *o*-carborane was synthesized. This group observed that the C-C distance between the carbons of the cluster increased from 1.624 Å to 1.829 Å once the amino groups were attached to the carborane.[30]

C-C bond lengths for substituted ortho-carborane are listed in Table 1. Inductive and resonance effects seem to dictate this negative hyperconjugation.[31] Due to the electron deficient nature of the carborane cluster, the carbons act as electron withdrawing groups, so substituents attached to the carbons of the carborane cage will act as electron donors. Since less electronegative elements have a better electron donating ability than more electronegative elements, substituents with less electronegative elements attached to the carbon will elongate the bond more.[31] Additionally, any substituent with an available lone

pair can form resonance structures (Scheme 1.6). Thus, these substituents are able to donate more electron density into the cluster than substituents that cannot. Since biscarborane has similar C-C bonds to *ortho*-carborane and reduces similarly compared to *ortho*-carborane, the C-C bond lengths of biscarborane should behave similarly to those of ortho-carborane. We hypothesize that, since the C-C bond is weaker with more donating substituents attached to the cluster, the clusters with longer C-C bonds will reduce more easily than unsubstituted carborane. Thus, these substituted carboranes may function better as electrolytes for flow batteries.

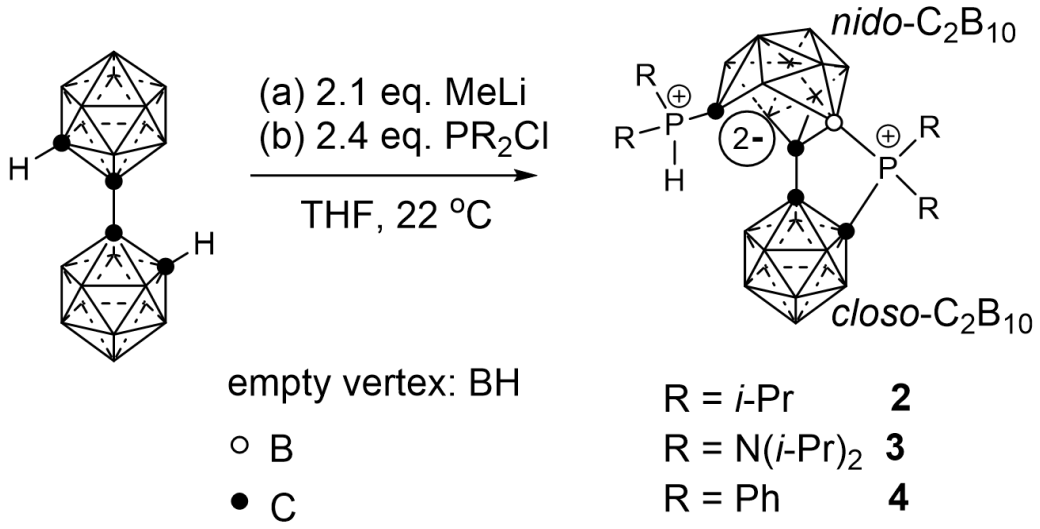
Table 1.1: C-C bond lengths found for different substituents. *The bond length for -NH_2 given in this table is a theoretical value, and the one listed in the paper is an actual value[31]

Substituent attached to *ortho*-carborane	C-C bond length (Å)
-H	1.624
-CH_3	1.663
-NH_2	1.86*
-OH	1.766
-F	1.663
-SiH_3	1.677
-PH_2	1.689
-SH	1.803
-Cl	1.692



Scheme 1.6. Resonance structures of substituted ortho-carboranes. represents any substituent with a lone pair, and the circular bond represents the rest of the carborane cluster[30]

1.4 Thiyl racidals



Scheme 1.7. Metal-free B-H bond activation of biscarborane with phosphine ligands.[32]

One interesting property of S-H bonds is that they can easily be homolytically cleaved to form thiyl radicals. These radicals can then participate in a variety of reactions, namely their addition to double[33,34] and triple bonds.[35] This relative ease of formation and high reactivity make thyil radicals promising reagents for various organic syntheses.[36] Thus, we wanted to form a new thiol compound to attempt these additions. In particular,

we wanted to form thiyl radicals on biscarborane due to its unusual interaction with different substituents. Previously, it was reported that when phosphine groups are attached to biscarborane, one phosphine group will perform a nucleophilic attack on a boron of the opposing carborane cluster, which caused the attacked cage to open (Scheme 1.4).[32] Thus, one B-H bond of a carborane cluster was activated without the use of a metal. This was the first reported case of this interaction occurring. We hypothesized that, in addition to their ability to add to alkenes and alkynes, thiyl radicals attached to biscarborane will perform a similar metal-free B-H bond activation compared to phosphine substituted biscarborane.

1.5 Nickel Complexes

Nickel has been utilized by the body as a metal center for catalysts for a variety of biological processes, such as a metal center in both carbon monoxide dehydrogenase (CODH) and Actyl CoA Synthase (ACS).[37] One use is acting as a metal center in (NiFe)-H_2-ases, which reversibly catalyzes the conversion of protons and electrons to hydrogen gas. The Ni-S bond is believed to play a role as part of the active site in the hydrogenase.[38] Due to this, we wanted to synthesize thiol-containing compounds to act as the active site for this reaction. Additionally, unspecified electron acceptors are present with these catalysts as well.[39] With this in mind, we wanted to synthesize a Ni complex that has a thiol-containing group that can accept electrons. These groups then donate the electrons back as needed. As shown previously, carboranes can act as reversible electron acceptors.[10] Thus, we hypothesize that a nickel complex with a thiol-functionalized carborane could act as good synthetic hydrogenase for the production of hydrogen gas.

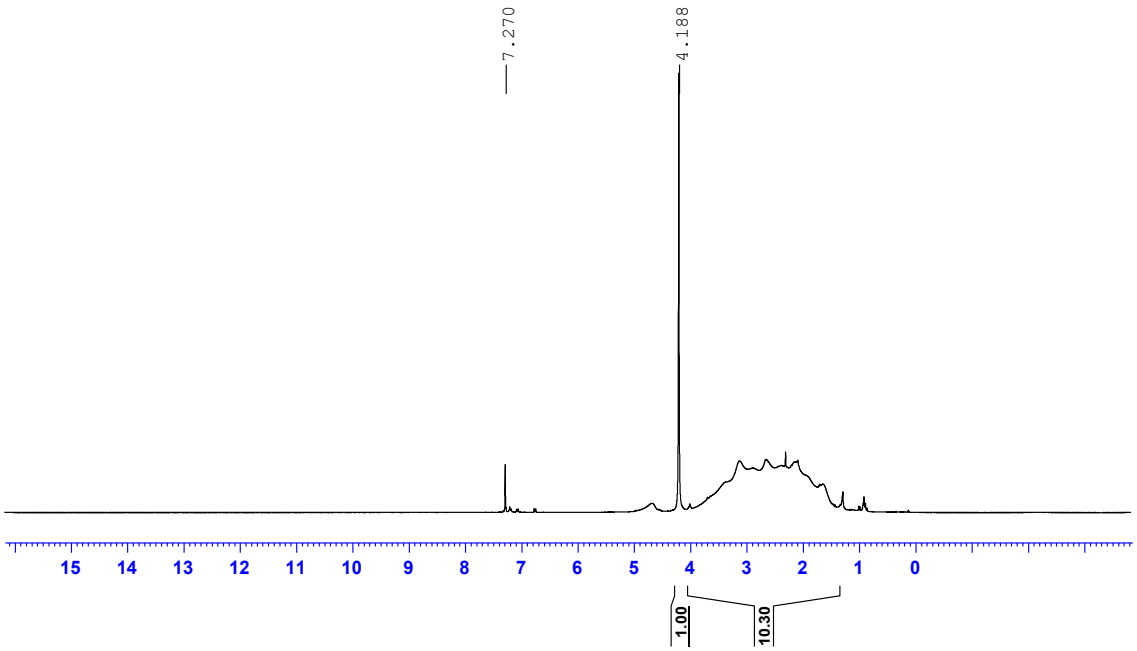
CHAPTER 2

EXPERIMENTAL

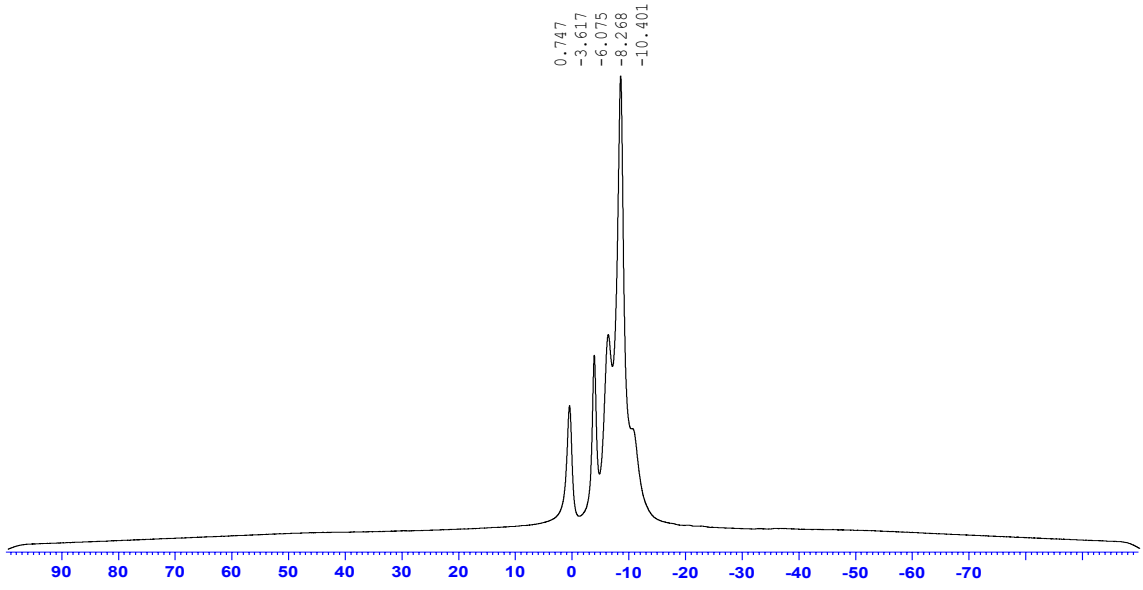
Biscarborane was synthesized according to a previously reported literature procedure.[14] Ortho-carborane, azobisisobutyronitrile, bis(triphenylphosphine)Ni(II) chloride, tetrabutyl ammonium bromide, and potassium bis(trimethyl)silyl amide were purchased and used without any modifications. All reactions (except the thiyl radical reactions) were performed under dry and air-free conditions until stated otherwise.

2.1 Synthesis of $(C_2B_{10}H_{10}SH)_2$

Biscarborane (50 mg, 0.523 mmol) was dissolved in tetrahydrofuran. Bis(trimethyl silyl) amide (0.7 M, 0.6 mL, 2.4 eq.) was then added dropwise to the solution under a nitrogen atmosphere, and the solution was allowed to stir overnight. The solvent was then removed, and the resulting solid was washed with hexane to remove excess base. Sulfur (12 mg, 0.26 eq) was then added to the solution, and the solution continued to stir for 22.5 hours at 60 °C to form the thiolate. The solution was exposed to air at this point. The solvent was then removed, and the resulting solid was washed with ether to remove impurities. Dichloromethane (15 mL) and hydrochloric acid (15 mL) were added to the remaining solid and stirred until all the solid dissolved. The organic layer was extracted with DCM from the aqueous layer, and the solvent was removed to obtain a brownish-white powder. (Yield 40%) ^{1}H NMR (300 MHz, $CDCl_3$): 4.192 (s, 1H). ^{11}B NMR (300 MHz, $CDCl_3$): -0.667 (s, 2B), -3.587 (s, 2B), -5.912 (s, 2B), -8.228 (s, 4B).



Spectrum 2.1. ^{1}H NMR spectrum for dithiol biscarborane.

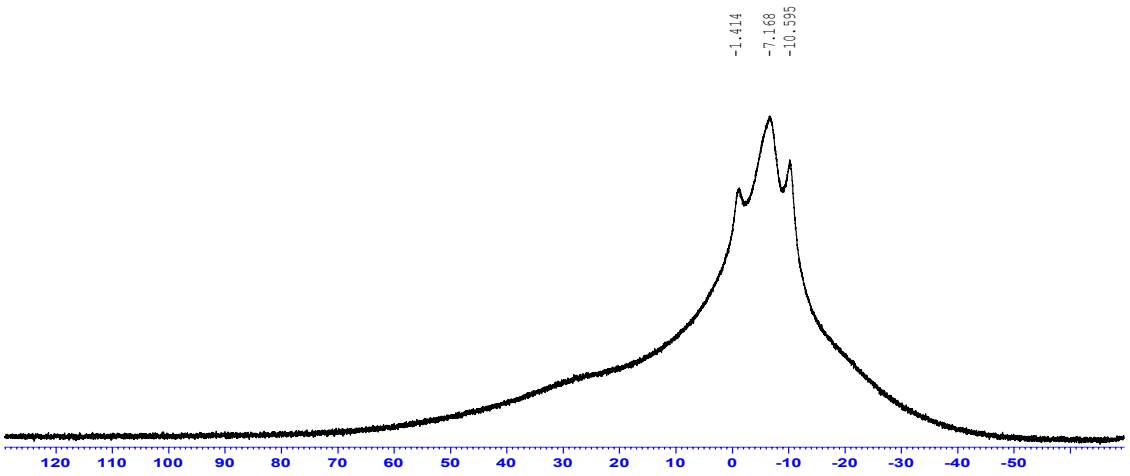


Spectrum 2.2. $^{11}B\{^{1}H\}$ NMR spectrum for dithiol biscarborane.

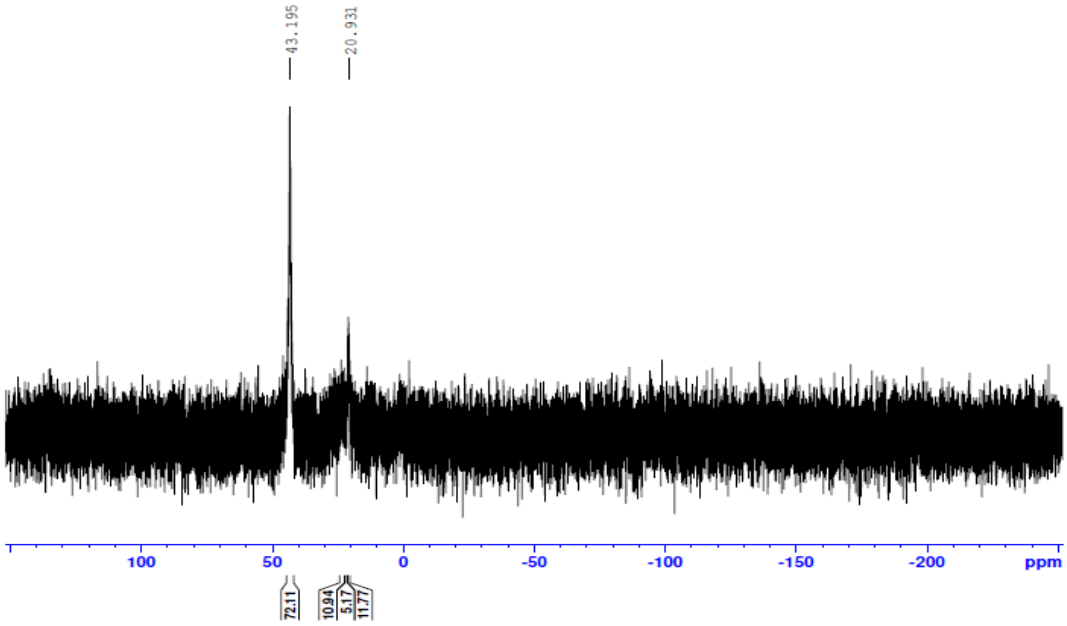
2.2 Synthesis of $(C_2B_{10}H_{10}SH)_2Ni(PPh_3)_2$

2,2'-dithiolate-1-1'-bis(*o*-carborane) (50 mg, 0.064 mmol) was dissolved in THF along with 1 eq. of $Ni(II)Cl_2(PPh_3)_2$ (42 mg, 0.064 mmol), and the solution was allowed to

stir for two days. The solvent was then removed, and the resulting solid was washed first with hexane and then with a hexane/toluene (1:2) mixture. The hexane/toluene mixture was dried away, which left an impure black solid material $^{31}P\{^{1}H\}$ NMR (300 MHz, $CDCl_3$): -43.44 (s) $^{11}B\{^{1}H\}$ NMR (300MHz, $CDCl_3$): -1.414 (s) , -7.168(s), -10.595 (s),



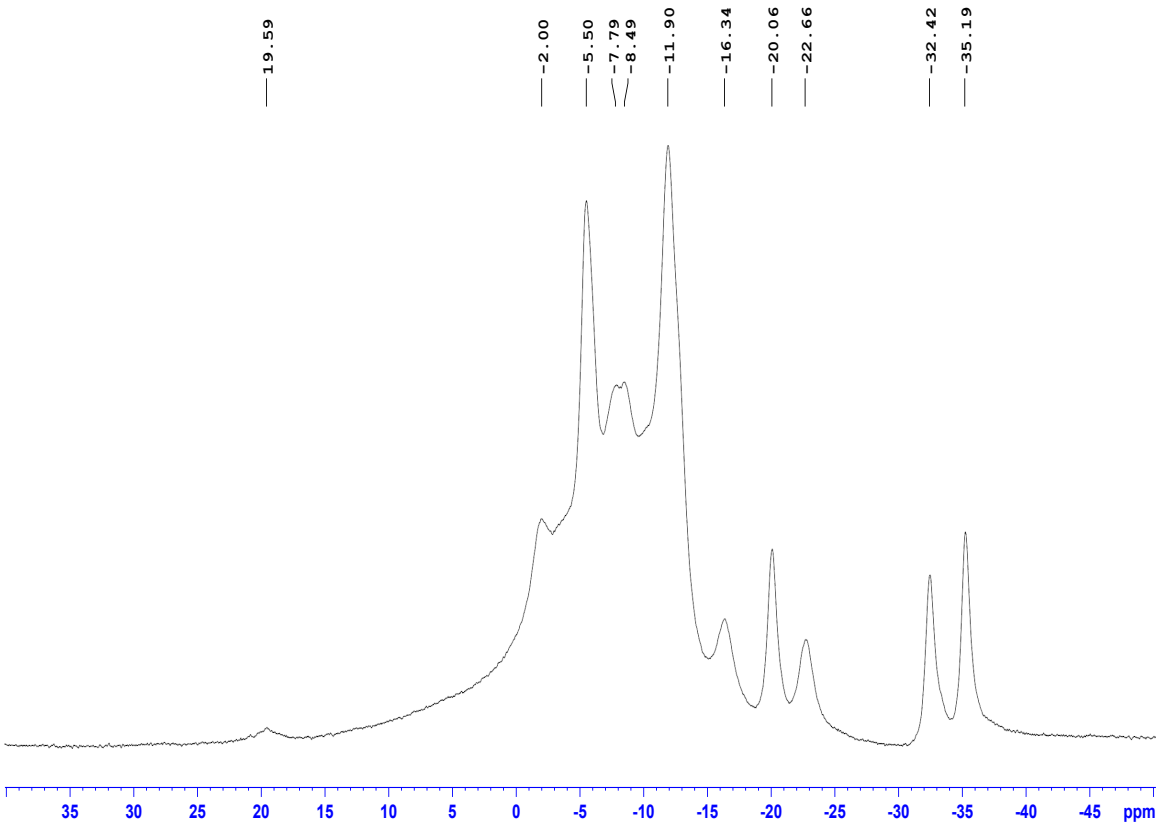
Spectrum 2.3. $^{11}B\{H\}$ NMR Spectrum for $(C_2B_{10}H_{10}SH)_2Ni(PPh_3)_2$



Spectrum 2.4. ^{31}P NMR spectrum for $(C_2B_{10}H_{10}SH)_2Ni(PPh_3)_2$

2.3 Reaction of dithiol with azobisisobutyronitrile

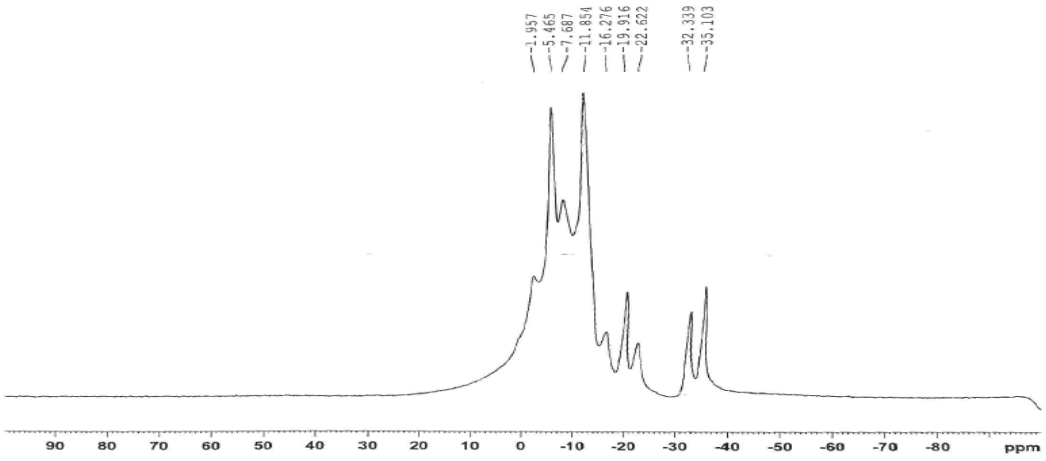
$(C_2B_{10}H_{10}SH)_2$ (50 mg, 0.14 mmol) was added to a solution of THF containing a catalytic amount of azobisisobutyronitrile (AIBN). This solution was stirred at 60 °C overnight. The THF was then removed which resulted in the formation of a white and yellow powder. This powder was then washed with hexane then DCM. Unfortunately, although the NMR indicates the formation of something that seemed to correlate to the productno crystals of this product were obtained. $^{11}B\{^1H\}$ NMR data (300 MHz, $CDCl_3$): 19.59 (s), -2.00 (s), -5.70 (s), -7.79 (s), -8.49 (s), -11.90 (s), -16.34 (s), -20.06 (s) -22.66 (s), -32.42 (s), -35.19 (s).



Spectrum 2.5. $^{11}B\{^1H\}$ NMR spectrum of the dithiol biscarborane after the addition of AIBN

2.4 Attempted addition of thiyl radical to 1-octene:

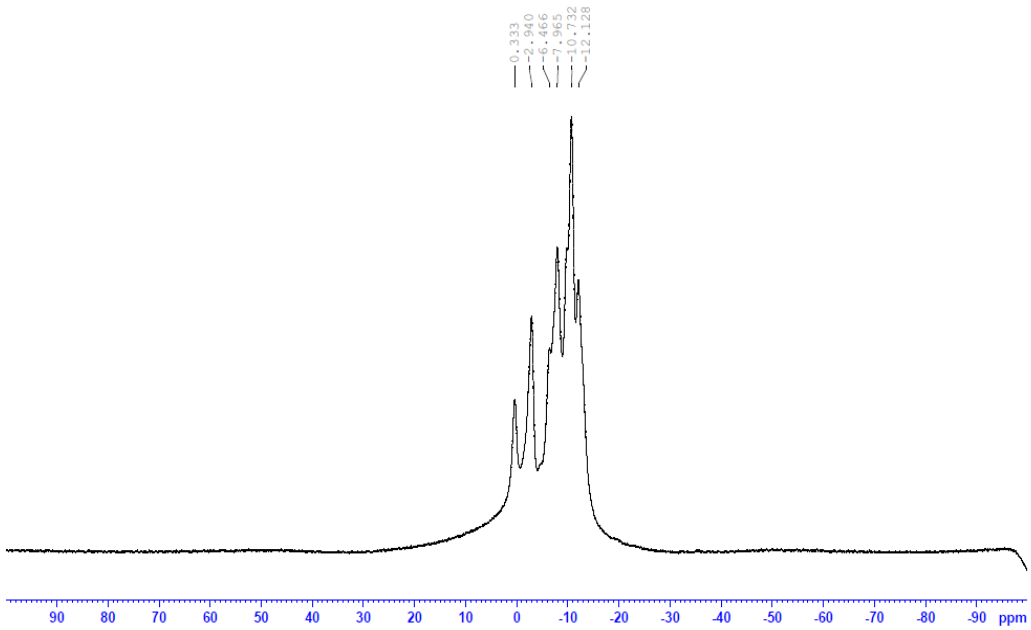
Dithiol biscarborane (20 mg, 0.056 mmol) was added along with 1-octene (9.26 μL, 0.12 mmol) and a catalytic amount of AIBN to THF. The following solution was stirred overnight at 60° C yielding a white and yellow powder. The product was washed with hexane and DCM. ^{11}B NMR data (300 MHz, $CDCl_3$): -1.957 (s), -5.465 (s), -7.687 (s), -11.854 (s), -16.916 (s), -22.622 (s), -32.339 (s), -35.103(s).



Spectrum 2.6. ^{11}B{^{1}H} NMR spectrum of the thyil radical reaction with 1-octene

2.5 Reduction of dithiol biscarborane using Mg:

Dithiol biscarborane (20 mg, 0.056 mmol) was added to THF along with metallic magnesium (1.39 mg, 0.056 mmol). This mixture was allowed to stir at room temperature overnight, which resulted in white and yellow powders. The compound was dissolved in THF and locked with $CDCl_3$ for NMR experiments. The compound was then washed with hexane followed by DCM, and both layers were used for crystallization. Unfortunately, no crystal structure was obtained for this reaction. NMR data: ^{11}B{^{1}H} (THF locked with $CDCl_3$): -0.333 (s), -2.940 (s), -6.466 (s), -7.965 (s), -10.732 (s), and -12.128 (s).



Spectrum 2.7. $^{11}B\{^{1}H\}$ NMR spectrum for the reduced dithiol biscarborane

2.6 Exchange of metalated thiolate with tetrabutyl ammonium bromide:

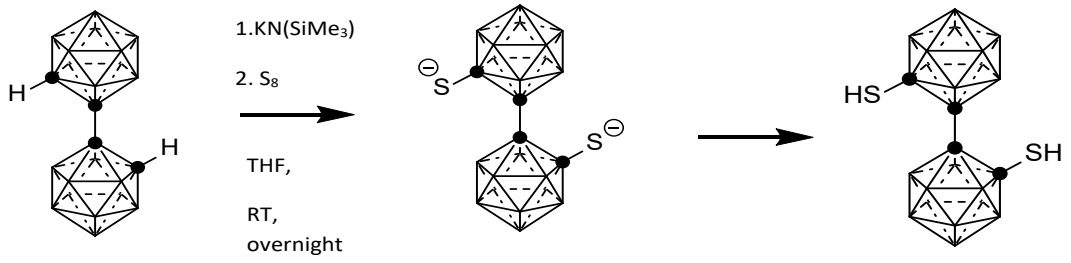
Dithiolate with potassium as a counterion (50 mg, 0.12 mmol) was dissolved in methanol along with tetrabutyl ammonium bromide (73 mg, 0.25 mmol) and this solution was allowed to sit at room temperature overnight. The methanol was the removed, an orange powder formed. This powder was then washed with hexane and then the powder was dissolved in THF. Slow evaporation in THF grew crystals of the product.

CHAPTER 3

RESULTS AND DISCUSSION

Synthesis of dimercaptan biscarborane and its anionic form.

To determine if bond elongation occurs in biscarborane, we wanted to synthesize biscarborane compounds with different substituents attached to the carbons of biscarborane. Thus, we successfully synthesized 1-1'-dimercaptan-bis-*o*-carborane (Figure 3.1) Upon characterization of the crystal structure, the C-C bond distances in each cage were found to be 1.858(3) Å compared to the C-C bond length of unsubstituted biscarborane (1.690(3) Å). Thus, the same bond elongation fueled by negative hyperconjugation is observed for biscarborane derivatives. To further show this, the anionic form of the dimercaptan biscarborane was also crystalized, and the crystal was characterized. The C-C bond length for the thiolate was 2.022(16) Å, which is much longer than the dimercaptan biscarborane C-C bonds, showing that the anionic form does have an enhanced donating ability.



Scheme 3.1. Synthesis of dithiol biscarborane

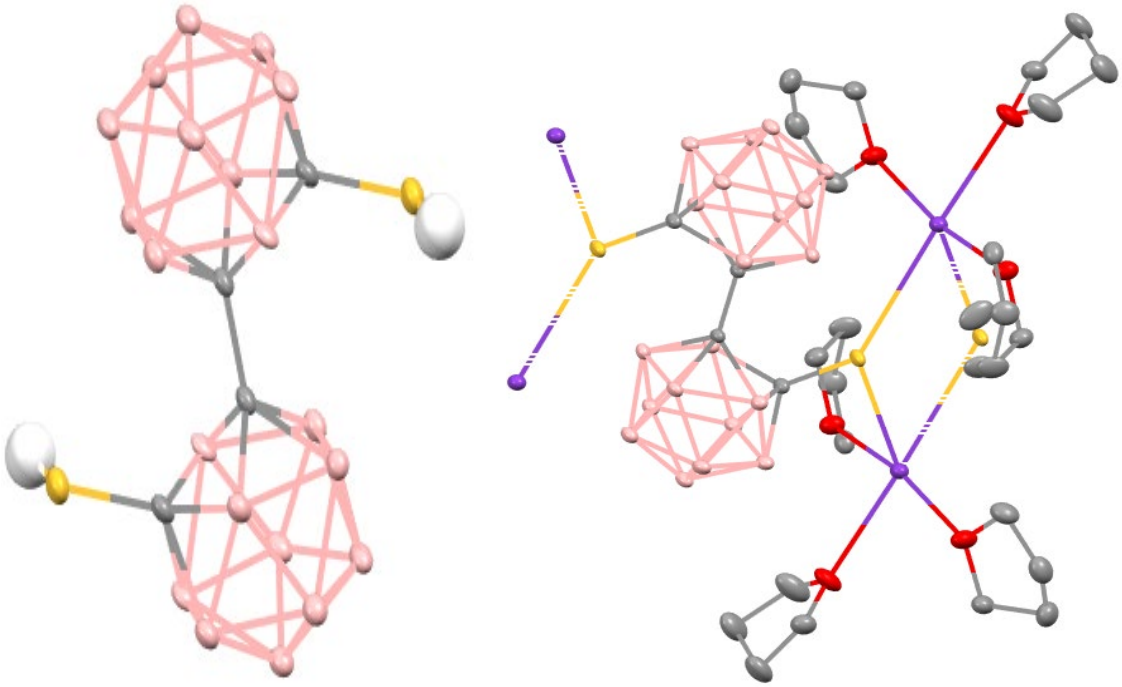


Figure 3.1. Crystal structure of dithiol biscarborane compound and its corresponding anion

Reduction of the thiol-biscarborane.

Cyclic Voltammetry (CV) experiments were performed on this compound to determine its reduction potentials. This CV was performed using a10 mM THF solution of the dimercaptan in a H-cell. Additionally, standard calomel electrode (SCE) was utilized as the standard electrode, a platinum electrode was utilized as the counter electrode, and a glassy carbon was utilized as the working electrode. After CV analysis, this compound was found to have two reversible reduction potentials at -1 and -1.8 vs. SCE. (Figure 2) This is consistent with other carboranes, which usually have a two-electron reduction as stated previously. Since the reduction potentials were both found to be reversible, then this compound can possibly be used as an electrolyte for flow batteries.

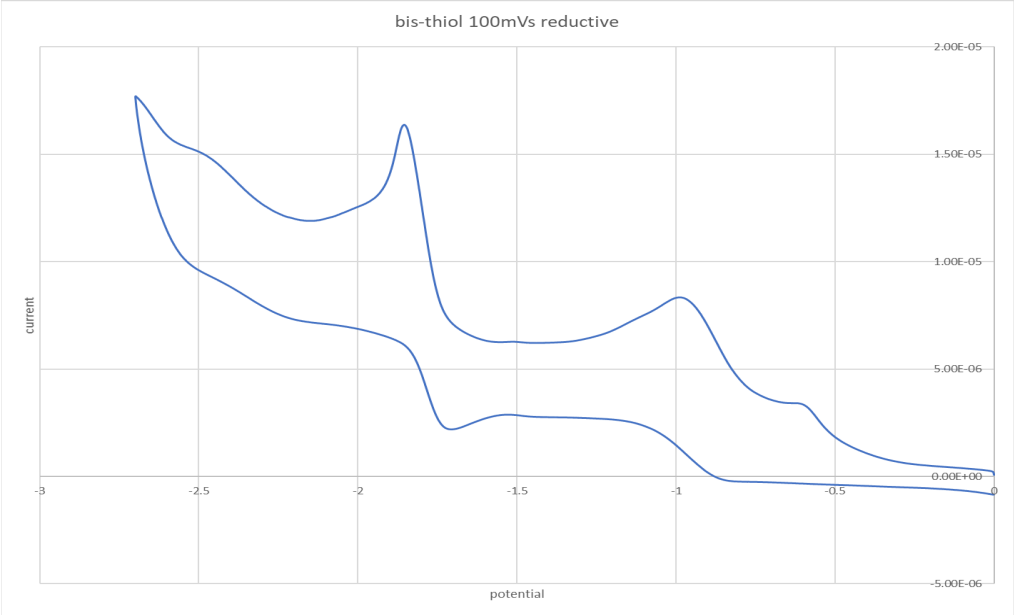


Figure 3.2. Cyclic voltammetry of the dithiol-biscarborane (100 mV/s)

Although the reduction of this compound is shown, it is unclear whether the reduction occurs within the cluster, which would mean that the electrons are delocalized within the carborane cluster, or the reduction is localized on the -SH substituent. Thus, the thiol biscarborane compound was reduced using magnesium metal, and NMR data was recorded for the compound. (Spectrum 2.7) Unfortunately, no crystal structure has yet been obtained for this.

Since the potassium counterion is coordinating directly to the sulfur anion, it may influence the sulfur's ability to donate electron density to the carborane cluster. To determine the full extent of the donating ability of the anionic form and to determine the effect that the potassium has on the donating ability of the sulfur anion an ion exchange reaction was performed to exchange the potassium cation with a noncoordinating cation, tetrabutyl ammonium. After stirring the anionic dimercaptan biscarborane and tetrabutuyl

ammonium bromide in methanol overnight, crystals were obtained for an anionic dimercaptan biscarborane molecule with tetra butyl ammonium as a counterion. The C-C bond distance for this molecule ranges between 2.03 (9)-2.06(10) Å, which was only slightly longer than 2.022(16) Å, which is the C-C bond distance than the bond distance observed when potassium acted as the counterion. However, the increase is very small, which indicates that the potassium counterion does not have a significant impact on the electronic character of the dimercaptan anion.

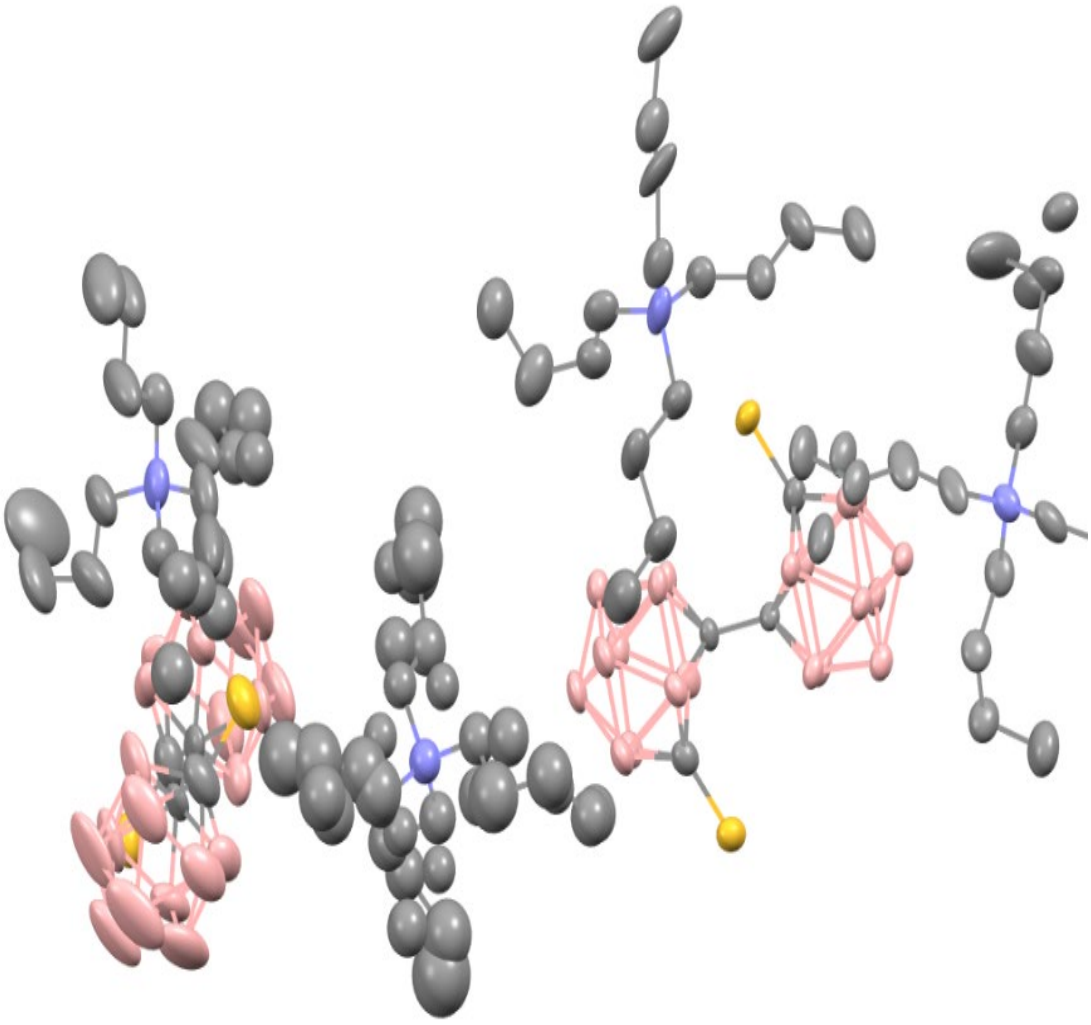


Figure 3.3. Crystal structure of $[(C_4H_9)_4N]^+ [(C_2B_{10}H_{10}S)_2]^-$. Hydrogen atoms omitted for clarity.

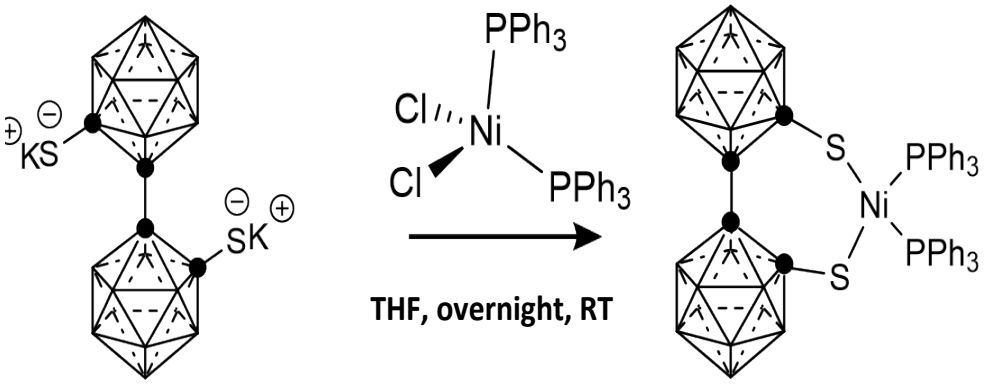
Biscarborane Thyil Radical Generation

To determine the interaction of thiyl radicals and the borons of biscarborane, dithiol biscarborane was added to a THF solution containing the radical initiator AIBN. After stirring this mixture overnight at 60 °C, the product shown in Spectrum 2.5 was formed, Unfortunately, no crystal structure of this product was obtained, so the exact nature of this product is still unknown. Additionally, this same reaction was done in the presence of 1-octene since thiyl radicals have been shown to add to double bonds. The resulting product was observed in Spectrum 2.5. This spectrum contains more peaks than the dimercaptan compound, which indicates that some of the symmetry of this compound has been lost. Additionally, the peaks at -32.42 and -35.19 indicate that one of the borons within the carborane cage have been removed from the cluster, so the product of this reaction could have an open face. This also indicates that the thiyl radical behaves differently than phosphines when attached to the biscarborane. Unfortunately, this product also did not form any crystals, so the exact nature of this product could not be determined.

Synthesis and Structure of the Nickel Biscarboranylthiolate Complex.

Since biscarborane seemed to be an attractive electron acceptor in hydrogenases, we wanted to synthesize a Ni metal complex that contained dimercaptan biscarborane as a ligand. Upon adding the thiolate form of the compound to bis(triphenylphosphine)Ni(II) chloride, the target product, $(C_2B_{10}H_{10}S)_2Ni(PPh_3)_2$, was formed (Figure 3.4). This compound adopted a slightly distorted square planar configuration. The Ni-S bond distances are 2.16(6)-2.17(6) Å, which fall into the shorter range of Ni-S bonds found for square-planar Ni-thiolate compounds (between 2.156 and 2.212Å).[38] Unfortunately,

although a crystal structure of this compound was obtained, any attempt to obtain a pure sample of this compound resulted in the decomposition of the Ni complex as observed through NMR spectroscopy. As a result, no further experiments or characterization could be performed for this compound.



Scheme 3.2 Synthesis of $(C_2B_{10}H_{10}SH)_2Ni(PPh_3)_2$

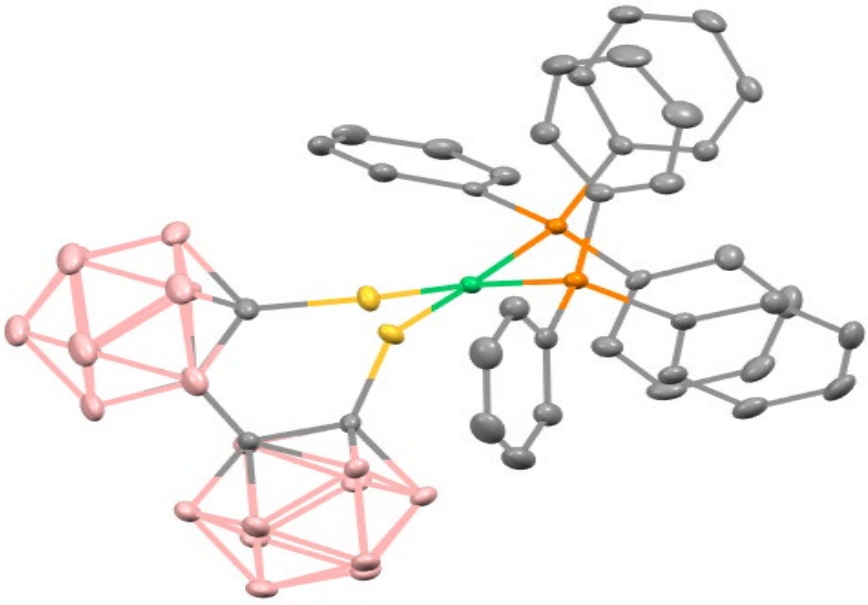


Figure 3.4. Crystal structure of $(C_2B_{10}H_{10}SH)_2Ni(PPh_3)_2$. Hydrogens omitted for clarity.

CHAPTER 4

CONCLUSION AND FUTURE WORK

In summary, a dithiol derivative of biscarborane was successfully synthesized. The C-C bond distances within the cluster did increase in the dithiol biscarborane opposed to unsubstituted biscarborane, suggesting that biscarborane has a similar negative hyperconjugation interaction with substituents compared to ortho-carborane. Cyclic voltammetry measurements have shown that this compound does retain a reversible two electron reduction that is usual for carborane compounds. Thus, this compound could potentially act as an electrolyte in flow battery systems. This compound seemed to have a reaction with the radical initiator AIBN, so this compound may form radials similarly to other thiols. A nickel complex that contains this substituted biscarborane molecule was also successfully synthesized.

There is still much work to do for these projects in the future. Although the carborane derivative has a two-electron reduction, stability of the compound both in solution and after repeated redox reactions still needs to be tested. Additionally, although the NMR data for the thyil radical reaction suggests that a reaction has occurred, the exact nature of this product has yet to be determined. A crystal structure of this compound should be obtained to determine if the product has activated a B-H bond similarly to the phosphorus derivative mentioned previously. Depending on the exact nature of this

product, the use of it as a reagent or as a ligand precursor could be explored. Finally, although a nickel complex with the thiol compound was synthesized, the compound was not successfully purified. In the future, a method to purify this compound needs to be found. Once the compound is pure, cyclic voltammetry of this compound needs to be done to find the reduction peaks of this compound to determine if this compound can reduce protons to hydrogen. Then, cyclic voltammetry of this compound should be performed again in acidic conditions to determine if there is any change in the reduction peak.

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